

NONCATALYTIC PROCESS FOR PRODUCING BIODIESEL FUEL
THAT DOES NOT GENERATE BY-PRODUCT

Technical Field

The present invention relates to a process for producing biodiesel fuel from vegetable or animal oils and fats or waste oils thereof (hereafter referred to as "wastes thereof") and methanol.

Background Art

Recently, environmental conservation awareness has increased, and thus, so-called "biodiesel fuel" produced from vegetable or animal oils and fats or wastes thereof has been increasingly used.

In general, biodiesel fuel refers to fuel that is mainly composed of fatty acid methyl esters obtained by subjecting triacylglycerol, which is a main component of vegetable or animal oils and fats or wastes thereof, to transesterification with methanol (hereafter referred to as a "methanolysis reaction").

The methanolysis reaction of triacylglycerol with methanol can be divided into three phases. In the first phase, a fatty acid methyl ester molecule and a diacylglycerol molecule are generated from a triacylglycerol molecule and a methanol molecule. In the second phase, a fatty acid methyl ester molecule and a monoacylglycerol molecule are generated from a diacylglycerol molecule and a methanol molecule. In the third phase, a fatty acid methyl ester molecule and a glycerin molecule are generated from a monoacylglycerol molecule and a methanol molecule.

In conventional processes for producing biodiesel fuel, the methanolysis reaction is completed following the third phase. Thus, glycerin is generated as a by-product. A variety of attempts have been made in order to make use of glycerin (see JP-A-2003-096473). However, there is a superfluous supply of glycerin in Japan. Given the present circumstances, glycerin is disposed in a dedicated-purpose incinerator. Disadvantageously, glycerin cannot be utilized as a heat source due to its low calorific

value. Although there is a strong demand for the production of biodiesel fuel without the generation of glycerin, there currently exists no such technique.

In the production of biodiesel fuel, the methanolysis reaction is generally carried out with the use of a catalyst such as an alkaline or acid catalyst. With a catalytic process, however, a catalyst (for example, sodium hydroxide) contaminates the reaction product. This necessitates neutralization and washing of the product and purging of the washing liquid.

An example of a process for producing biodiesel fuel without the use of a catalyst is a technique that utilizes a supercritical fluid (see D. Kusdiana, S. Saka, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, *Fuel*, 80 (2001), 225-231; and D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, *J. of Chem. Eng. of Japan*, 34(3), 383-387, 2001), No. 3, *Jasco Report*, pp. 28-31, May 28, 1999). With this technique, however, glycerin is still generated as a by-product.

Summary of the Invention

An object of the present invention is to provide a process for producing biodiesel fuel from vegetable or animal oils and fats or wastes thereof and methanol that does not utilize a catalyst and that does not generate glycerin as a by-product.

More specifically, the present invention includes the following inventions.

(1) A process for producing biodiesel fuel, wherein vegetable or animal oils and fats or wastes thereof are mixed with methanol, and a methanolysis reaction is carried out without the use of a catalyst under reaction conditions where glycerin is not generated.

(2) The process according to (1) above, wherein the reaction conditions where glycerin is not generated constitute a reaction temperature of between 370°C and 500°C, a reaction pressure of between 20 MPa and 60 MPa, and a reaction period of between 4 minutes and 12 minutes.

(3) The process according to (1) above, wherein degradation of a carbon chain in a fatty acid group is carried out in parallel with the methanolysis reaction.

(4) The process according to (1) above, wherein the vegetable or animal oils and fats or wastes thereof are mixed with methanol at a volume ratio of 1:2 to 2:1.

(5) The process according to (1) above, wherein the methanolysis reaction is carried out in a Hastelloy reaction tube in which adequate mixing conditions can be maintained.

(6) Biodiesel fuel that is mainly composed of fatty acid methyl esters, monoacylglycerol, and diacylglycerol.

This specification includes part or all of the contents as disclosed in the specifications of Japanese Patent application No. 2003-294521, which are the base of the priority claim of the present application.

Brief Description of the Drawing

Fig. 1 schematically shows an example of an apparatus for producing biodiesel fuel according to the present invention.

Each number in Fig. 1 means the following.

1 --- tank 1 for starting materials (for vegetable or animal oils and fats)

2 --- delivery pump (for vegetable or animal oils and fats)

3 --- tank 2 for starting materials (for methanol)

4 --- delivery pump (for methanol)

5 --- preheating tube

6 --- heater for preheating tube

7 --- reaction tube

8 --- heater for reaction tube

9 --- cooling tube

10 -- pressure-releasing valve

11 -- decompression tank

12 -- decompression pump

13 -- line for recovering excess methanol

14 -- chiller (or device for recovering methanol)

15 -- outlet for biodiesel fuel

Preferred Embodiments of the Invention

In the present invention, various conditions for a methanolysis reaction are adequately regulated, thereby completing the reaction in the first phase while inhibiting the reaction in the third phase. Thus, biodiesel fuel can be produced without generating glycerin. The reaction in the second phase may proceed adequately. As the reaction in the second phase makes progress, however, the concentration of diacylglycerol in the resulting biodiesel fuel is lowered, the concentration of monoacylglycerol is elevated, and the viscosity of the biodiesel fuel is lowered. Thus, various conditions for the methanolysis reaction are preferably regulated so as to accelerate the reaction in the second phase.

A noncatalytic process can be accomplished by carrying out the methanolysis reaction under supercritical conditions.

Since no by-product is generated, the biodiesel fuel yield can be enhanced. Preferably, the yield can be substantially 100% of the starting oil, whereas such yield was approximately 80% in the past.

The biodiesel fuel produced by the process according to the present invention is mainly composed of fatty acid methyl esters, diacylglycerol, and monoacylglycerol. In contrast, biodiesel fuel produced by the conventional technique is mainly composed of

fatty acid methyl esters and does not substantially contain diacylglycerol or monoacylglycerol.

Vegetable or animal oils and fats comprise a large quantity of long chain fatty acids having 16 or more carbon atoms. In general, the viscosity of diacylglycerol or monoacylglycerol comprising a long chain fatty acid group is higher than that of fatty acid methyl esters. Therefore, such substance is often unsuitable for biodiesel fuel.

The present invention can provide biodiesel fuel having sufficient viscosity as biodiesel fuel through the process described below. That is, degradation of a carbon chain in a fatty acid group is carried out in parallel with a methanolysis reaction to convert a long chain fatty acid group to a medium chain fatty acid group having approximately 6 to 12 carbon atoms. This lowers the viscosity of a mixture mainly composed of fatty acid methyl esters, diacylglycerol, and monoacylglycerol.

Further, the present invention relates to biodiesel fuel that is mainly composed of fatty acid methyl esters, monoacylglycerol, and diacylglycerol. The term "mainly composed of" means that the biodiesel fuel comprises at least 40% fatty acid methyl esters by weight, at least 10% monoacylglycerol by weight, and at least 5% diacylglycerol by weight. Biodiesel fuel according to the present invention preferably comprises 40% to 60% fatty acid methyl esters by weight, 10% to 30% monoacylglycerol by weight, 5% to 20% diacylglycerol by weight, 5% to 20% other aliphatic compounds by weight, and less than 1% each triacylglycerol and glycerin by weight. "Other aliphatic compounds" are described below. More preferably, biodiesel fuel has a cetane number of 49 to 65, a flash point of 100°C to 200°C, kinematic viscosity at 30°C of 3 mm²/sec to 20 mm²/sec, and a pour point of -5°C or lower.

The present invention is hereafter described in greater detail.

1. Starting material

The methanolysis reaction according to the present invention employs a mixture of vegetable or animal oils and fats or wastes thereof and methanol as a starting material. Examples of vegetable oils that can be used in the present invention include, but are not

limited to, rapeseed oil, canola oil, corn oil, soybean oil, sunflower oil, and safflower oil. Examples of animal oils and fats that can be used in the present invention include, but are not limited to, porcine fat (lard) and beef tallow. The term "waste oils" refers to vegetable or animal oils and fats that are to be disposed due to deterioration in their qualities after they have been used for cooking in, for example, households, restaurants, fast food restaurants, or factories for meals. Examples of wastes of vegetable or animal oils and fats that can be used in the present invention include, but are not limited to, waste oils that had been used for cooking, such as deep-fried foods, pork cutlets, or fried chicken.

The mixing ratio of the vegetable or animal oils and fats or wastes thereof to methanol can be appropriately selected. Preferably, the vegetable or animal oils and fats or wastes thereof are mixed with methanol at a volume ratio of 1:2 to 2:1.

2. Reaction conditions

The methanolysis reaction according to the present invention is carried out without the use of a catalyst under reaction conditions where glycerin is not generated.

The aforementioned "reaction conditions where glycerin is not generated" can be any conditions as long as the condition that "glycerin is not generated" is satisfied. In the present invention, "reaction conditions where glycerin is not generated" include reaction conditions where substantially no glycerin is generated as well as reaction conditions where no glycerin is generated. "Reaction conditions where substantially no glycerin is generated" refers to the reaction conditions where glycerin is generated but the generated glycerin is not separated from the biodiesel fuel. Cases where "the generated glycerin is not separated from the biodiesel fuel" include, but are not limited to, cases where the amount of glycerin generated is so small that the glycerin is not separated from the biodiesel fuel and cases where the lipophilic property of the generated glycerin is enhanced by further reaction (such as substitution of OH with methyl) and thus is not separated from the biodiesel fuel. Under the aforementioned reaction conditions, the reaction temperature is preferably between 370°C and 500°C, and more preferably between 380°C and 450°C; the reaction pressure is preferably

between 20 MPa and 60 MPa, more preferably between 30 MPa and 50 MPa, and most preferably 40 MPa; and the reaction period is preferably between 4 minutes and 12 minutes. More preferably, the temperature of the mixture to be poured into a reaction tube in which the reaction is carried out is at least 250°C.

Degradation of a carbon chain in a fatty acid group is preferably carried out in parallel with the aforementioned methanolysis reaction. "Degradation of a carbon chain in a fatty acid group" refers to a reaction where long chain fatty acid groups (having 14 or more carbon atoms) richly contained in vegetable or animal oils and fats or wastes thereof are converted to medium chain fatty acid groups (having approximately 6 to 12 carbon atoms). Reaction conditions are not particularly limited. When vegetable or animal oils and fats or wastes thereof are mixed with methanol, and the methanolysis reaction is carried out at a reaction temperature of between 390°C and 500°C, and preferably between 390°C and 450°C; a reaction pressure of between 20 MPa and 60 MPa, preferably between 30 MPa and 50 MPa, and most preferably 40 MPa; and a reaction period of between 4 minutes and 12 minutes, for example, degradation of a carbon chain in a fatty acid group proceeds in parallel with the methanolysis reaction. More preferably, the temperature of the mixture to be poured into the reaction tube in which the reaction is carried out is at least 250°C. The mechanism of converting long chain fatty acid groups to medium chain fatty acid groups has not yet been elucidated. For example, long chain fatty acid groups are considered to be converted to medium chain fatty acid groups through the cleavage of unsaturated bonds in the long chain fatty acid groups caused at high temperature and high pressure. A variety of substances can constitute other "cleaved ends" after the cleavage. Examples thereof include hydrocarbons, fatty acids, and fatty alcohols having approximately 6 to 12 carbon atoms. Such "cleaved ends" may be incorporated in biodiesel fuel as a final product.

After the completion of the methanolysis reaction, the reaction mixture is heated under reduced pressure to remove unreacted methanol therefrom by vaporization. Thus, biodiesel fuel as a final product can be obtained. Preferably, the removed methanol is recovered by cooling and then used again in the methanolysis reaction as a starting material.

3. Reaction apparatus

In the present invention, the methanolysis reaction can be carried out in any reaction vessel as long as the aforementioned reaction conditions are satisfied. Preferably, the methanolysis reaction is carried out in a Hastelloy reaction tube in which adequate mixing conditions can be maintained. More preferably, the methanolysis reaction is carried out in a Hastelloy reaction tube with uniformly-heated interior conditions, a sufficient length for the reaction, and adequate mixing conditions. Examples of metal materials for reaction vessels or reaction tubes that are commonly used in the apparatuses for supercritical reactions include stainless steel, Hastelloy, and Inconel. In the method according to the present invention, an apparatus made of Hastelloy is preferable because of the following reasons. An apparatus made of stainless steel may not be able to resist high temperatures or high pressures. In an apparatus made of Inconel, the reaction may proceed disadvantageously, which could result in the generation of glycerin. There exist a variety of types of Hastelloy, such as Hastelloy A, B, C, and F. Any of these can be used in the present invention, and Hastelloy C is usually used. Specific examples of Hastelloy C that can be used in the present invention are HC-22 and HC-276 (Mitsubishi Materials Corporation). The "reaction tube with uniformly-heated interior conditions" refers to a reaction tube wherein the temperature therein can be maintained at a substantially uniform level so that the methanolysis reaction can proceed uniformly. The "reaction tube with a sufficient length for the reaction" refers to a reaction tube having a length sufficient for securing the reaction period necessary for obtaining biodiesel fuel with an adequate composition. If the reaction tube is too short, the methanolysis reaction cannot proceed sufficiently because the sufficient reaction period cannot be secured. Thus, biodiesel fuel with an adequate composition cannot be obtained. The "reaction tube with adequate mixing conditions" refers to a reaction tube that can maintain mixing conditions under which the methanolysis reaction proceeds uniformly without generating glycerin as a by-product. More specifically, it refers to a reaction tube that can maintain mixing conditions by means of the flow of the supercritical fluid itself without

the aid of a stirring means (e.g., a static mixer). When a general stirring means is employed, stirring is likely to become excessively strong, and glycerin is likely to be generated as a by-product if the stirring is strong. More preferably, the methanolysis reaction is carried out in a reaction tube made of Hastelloy, which has an inner diameter of between 1.8 mm and 7.0 mm, a length of between 0.5 m and 15 m, and an interior volume of between 14 ml and 600 ml. The aforementioned reaction tube can be used in any form. For example, it may be linear, wound into a coil form, or folded into a hairpin form. Typically, the methanolysis reaction is carried out in a coil form reaction tube made of Hastelloy C, which has an inner diameter of 1.8 mm, a length of 8 m, and an interior volume of 20 ml.

An example of the reaction apparatus comprising such reaction tube is schematically shown in Fig. 1. With the use of this apparatus, starting materials can be adequately mixed with each other by means of a mixer before heating, which enables the apparatus to be continuously and stably operated. The mixer is preferably a T-type mixer in which the ratio of the total channel area before mixing to that after mixing is 2:1. With the use of this apparatus, unreacted methanol can be heated under reduced pressure, recovered through vaporization, and then used again as a starting material.

4. Reaction product

The biodiesel fuel produced by the method according to the present invention preferably comprises 40% to 60% fatty acid methyl esters by weight, 10% to 30% monoacylglycerol by weight, 5% to 20% diacylglycerol by weight, 5% to 20% other aliphatic compounds by weight, and less than 1% each triacylglycerol and glycerin by weight. The term "other aliphatic compounds" used herein is a generic term for compounds, such as aliphatic compounds derived from glycerin, in which glycerin generated during the methanolysis reaction is subjected to further reaction, such as substitution of OH with methyl, "cleaved ends" generated upon the conversion of the long chain fatty acid group to the medium chain fatty acid group (e.g., hydrocarbons, fatty acids, and fatty alcohols having approximately 6 to 12 carbon atoms), and aliphatic compounds comprising free fatty acids resulting from other causes.

Compositions of the biodiesel fuel (contents of fatty acid methyl esters, monoacylglycerol, diacylglycerol, triacylglycerol, glycerin, and other aliphatic compounds) were analyzed by gas chromatography-mass spectrometry under the following conditions. The Agilent gas chromatography 6890N system (Agilent Technology) and the GC-mate II mass spectrometer (JEOL Datum Ltd.) were employed. The HP-5TA column (15 m x 0.32 mm x 0.1 μ m, Agilent Technology) was also employed. Helium was used as a carrier gas (flow rate: 1.5 ml/min). The oven temperature was held at 50°C for 1 minute at the time of the initiation of analysis, elevated to 250°C at 10°C/min, further elevated to 365°C at 15°C/min, and held at 365°C for 8 minutes. The inlet temperature was 220°C, the split ratio was 45:1, and the amount of the sample injected was 2 μ l. The analyte was diluted to approximately 20 mg/ml with the aid of 1-butanol. Based on the obtained mass spectra, the component was identified, and the content thereof was determined based on the peak area in the gas chromatogram. Tridecanoic acid methyl ester or ethylene glycol was used as the internal standard.

Under the above conditions, the composition of a fatty acid group cannot be analyzed. Thus, gas chromatography-mass spectrometry was carried out under the following conditions to analyze the fatty acid composition of fatty acid methyl esters contained in the biodiesel fuel. The HP-INNOWax column (cross-linked PEG, 30 m x 320 μ m x 0.5 μ m, Agilent Technology) was installed in the aforementioned apparatus, and helium was used as a carrier gas (flow rate: 1.5 ml/min). The oven temperature was held at 150°C for 1 minute at the time of the initiation of analysis, elevated to 200°C at 15°C/min, further elevated to 250°C at 2°C/min, and then held at 250°C for 5 minutes. The inlet temperature was 220°C, the split ratio was 45:1, and the amount of the sample injected was 2 μ l. The analyte was diluted to approximately 20 mg/ml with the aid of 1-butanol. Based on the obtained mass spectra, the type of fatty acid was identified, and the content thereof was determined based on the peak area in the gas chromatogram. Tridecanoic acid methyl ester was used as the internal standard. In the biodiesel fuel produced by the method according to the present invention, the fatty acid compositions in fatty acid methyl esters are considered to be substantially the same as the compositions of fatty acid groups contained in all the molecular species constituting the

aforementioned biodiesel fuel. This is because the methanolysis reaction in a supercritical fluid proceeds without being affected by the chain length of fatty acid.

The biodiesel fuel produced by the method according to the present invention preferably has a cetane number of 49 to 65, a flash point of 100°C to 200°C, kinematic viscosity at 30°C of 3 mm²/sec to 20 mm²/sec, and a pour point of -5°C or lower.

The cetane number was measured in accordance with the method specified in JIS K 2280, the pour point was measured in accordance with the method specified in JIS K 2269, the kinematic viscosity (30°C) was measured in accordance with the method specified in JIS K 2283, and the flash point (PMCC test) was measured in accordance with the method specified in JIS K 2265.

[Example 1]

According to the procedure described below, biodiesel fuel was produced from commercially available canola oil using the apparatus shown in Fig. 1. A coil form HC-22 reaction tube (Hastelloy C; inner diameter: 1.8 mm; length: 7.8 m; interior volume: approximately 20 ml; Mitsubishi Materials Corporation) was used.

Canola oil (Oilio[®], Nisshin OilIIO, Ltd.) was placed in a tank 1 for starting materials and methanol (reagent chemicals, Wako Pure Chemical Industries, Ltd.) was placed in a tank 2 for starting materials. A delivery pump was adjusted so that the mixing ratio of canola oil to methanol became 2:1. The temperature in the reaction tube was 395°C, the pressure therein was 40 MPa, the time necessary for passing through the reaction tube was 4 minutes, and the temperature at the time of injection was 270°C. Given the circumstances, the resulting biodiesel fuel was comprised of approximately 50% various fatty acid methyl esters by weight, approximately 25% monoacylglycerol by weight, approximately 20% diacylglycerol by weight, approximately 5% other aliphatic compounds by weight, and less than 1% each triacylglycerol and glycerin by weight. Further, the biodiesel fuel had a cetane number of 51.6, a flash point (PMCC test) of 136°C, kinematic viscosity of 15.10 mm²/sec, and a pour point of -5°C. These fuel properties were substantially the same as those of common biodiesel fuel derived from rapeseed. Furthermore, the fatty acid compositions of the fatty acid methyl esters

in the biodiesel fuel were as follows: 55% oleic acid (C18:1) by weight; 16% linoleic acid (C18:2) by weight; 5% stearic acid (C18:0) by weight; 12% palmitic acids (C16:0 and C16:1) by weight; 7% eicosanoic acids (C20:0, C20:1, and C20:2) by weight, and 5% medium chain fatty acids (C6 to C12) by weight.

[Example 2]

According to the procedure described below, biodiesel fuel was produced from waste cooking oil discharged from households using the apparatus shown in Fig. 1. A coil form HC-22 reaction tube (inner diameter: 1.8 mm; length: 7.8 m; interior volume: approximately 20 ml) was used.

First, large impurities such as residues remaining after deep-frying were exclusively removed from waste cooking oil discharged from households without pretreatment, such as dehydration or removal of free fatty acids. A delivery pump was adjusted so that the volume ratio of the waste cooking oil to methanol became 2:1.

The temperature inside the reaction tube was 380°C, the pressure therein was 40 MPa, the time necessary for passing through the reaction tube was 4 minutes, and the temperature at the time of injection was 270°C. Given the circumstances, the product had a coefficient of viscosity of 24.3 mPa*sec. This value was larger than that of common biodiesel fuel (8.6 mPa*sec). The coefficient of viscosity was measured at 23°C using CVJ5000 (AND). The fatty acid compositions of the fatty acid methyl esters in the biodiesel fuel were as follows: 64% oleic acid (C18:1) by weight; 1% linoleic acid (C18:2) by weight; 13% stearic acid (C18:0) by weight; 14% palmitic acid (C16:0) by weight; 3% eicosanoic acids (C20:0, C20:1, and C20:2) by weight, and 5% medium chain fatty acids (C6 to C12) by weight.

The temperature inside the reaction tube was 450°C, the pressure therein was 40 MPa, the time necessary for passing through the reaction tube was 4 minutes, and the temperature at the time of injection was 270°C. Given the circumstances, the product had a lowered coefficient of viscosity of 9.16 mPa*sec. The fatty acid compositions of the fatty acid methyl esters in the biodiesel fuel were as follows: 60% oleic acid (C18:1) by weight; 0.6% linoleic acid (C18:2) by weight; 11% stearic acid (C18:0) by weight;

14% palmitic acid (C16:0) by weight; 2% eicosanoic acids (C20:0, C20:1, and C20:2) by weight, and 12% medium chain fatty acids (C6 to C12) by weight.

[Example 3]

According to the procedure described below, biodiesel fuel was produced from commercially available lard using the apparatus shown in Fig. 1. A coil form HC-22 reaction tube (inner diameter: 1.8 mm; length: 7.8 m; interior volume: approximately 20 ml) was used.

Lard (high-quality lard; fat content: 99.5%; Miyoshi Oil & Fat Co., Ltd.) was placed into a tank 1 for starting materials, and the content of the tank was heated and maintained at 60°C in order to improve the fluidity. Methanol (reagent chemicals, Wako Pure Chemical Industries, Ltd.) was placed in a tank 2 for starting materials. A delivery pump was adjusted so that the mixing ratio of lard to methanol became 1:2. The temperature in the reaction tube was 500°C, the pressure therein was 40 MPa, the time necessary for passing through the reaction tube was 8 minutes, and the temperature at the time of injection was 300°C. Given the circumstances, the resulting biodiesel fuel was comprised of 56% various fatty acid methyl esters by weight, 20% monoacylglycerol by weight, 10% diacylglycerol by weight, 14% other aliphatic compounds by weight, and less than 1% each triacylglycerol and glycerin by weight (undetectable). Further, the fatty acid compositions of the fatty acid methyl esters in the biodiesel fuel were as follows: 10% oleic acid (C18:1) by weight; 25% stearic acid (C18:0) by weight; 33% palmitic acid (C16:0) by weight; 23% medium chain fatty acids (C6 to C12) by weight; 4% myristic acid (C14:0) by weight; 1.3% heptadecanoic acid (C17:0) by weight; and 2.2% other fatty acids (C3, C15, and C20) by weight.

When biodiesel fuel was produced from lard in accordance with a conventional technique utilizing an alkaline catalyst, the fuel was solidified at approximately 10°C. On the contrary, the biodiesel fuel produced by the method described in this Example was not solidified even at 0°C.

Industrial Applicability

According to the present invention, biodiesel fuel can be produced without generating glycerin as a by-product. Specifically, a more advanced carbon-cycle energy system can be constructed according to the present invention. Since no by-product is produced in the present invention, the biodiesel fuel yield can be enhanced. Further, a noncatalytic technique can eliminate the need for pretreatment of a starting material, for neutralization and washing of products, and for purging of washing liquid, which had been essential in conventional production techniques.

All the publications, patents and patent applications cited herein are incorporated herein by reference in their entirety.